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Fluoride removal from ground water using magnetic and nonmagnetic corn stover biochars

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ABSTRACT

Slow pyrolysis corn stover biochar was prepared at 500 °C in an ingeniously developed reactor. Biooil was also collected. Corn stover biochar was magnetized by mixing aqueous biochar suspension with aqueous Fe^{3+}/Fe^{2+} solution, followed by NaOH treatment. Corn stover biochar (CSBC) and magnetic corn stover biochar (MCSBC) were characterized by pHzpc, S_{BET}, X-ray, FT-IR, SEM, SEM-EDX, TEM, EDXRF and Raman analyses. Magnetic moment of MCSBC was also measured. Both the biochars were utilized for fluoride removal to replace the existing commercially available costly adsorbents. Maximum fluoride removal was achieved at pH 2.0. Adsorption studies were carried out at 25, 35 and 45 °C. Fluoride removal on CSBC and MCSBC was decreased with rise in temperature [CSBC: Q^0_{25} = 6.42 mg/g; Q^0_{35} = 5.17 mg/g; Q^0_{25} = 4.99 mg/g and MCSBC: Q^0_{25} = 4.11 mg/g; Q^0_{35} = 3.45 mg/g; Q^0_{25} = 3.41 mg/g]. Pseudo-first order kinetics best fit the fluoride adsorption data. Both biochars successfully remediated fluoride from contaminated ground water.

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1. Introduction

Fluoride presence in ground water is a natural process. It is influenced by local/regional geological and hydrogeological conditions. Fluoride is one of the essential elements for human health. It is beneficial if present up to 1.0 mg/L. The World Health Organization and Bureau of Indian Standards have set the maximum permissible limit of 1.5 mg/L in potable water (BIS, 1991; WHO, 2006). Fluoride contamination is reported in India, China, Norway, USA, and UK (Ayoob and Gupta, 2006; Dou et al., 2012; Mohan et al., 2012). Fluoride contamination was reported in different Indian states including Rajasthan, Andhra Pradesh, Gujarat, Assam, Haryana, Jharkhand, Karnataka, Madhya Pradesh, and Uttar Pradesh (CGWB, 2010; Mohan et al., 2012).

High fluoride concentration in ground water is due to the weathering of fluorospars (CaF_2), fluorapatite [$Ca_5(PO_4)_3F$] and cryolite (Na_3AlF_6) present in the earth's crusts and also due to the volcanic and fumarolic processes (Mohan et al., 2012).

In the absence of alternate source, drinking water defluoridation is the only suitable option to mitigate fluoride contamination. Water defluoridation methods include adsorption (Paudyal et al., 2013; Sinha et al., 2003; Sivasamy et al., 2001), ion-exchange (Chubar et al., 2005), precipitation (Turner et al., 2005), and reverse osmosis (Sehn, 2008). Bone char (Brunson and Sabatini, 2014; Leyva-Ramos et al., 2009), activated alumina (Bouguerra et al., 2007) and hydrous zirconium oxide (Dou et al., 2012) were used for fluoride removal. Various other adsorbents applied for fluoride removal were reviewed (Ayoob and Gupta, 2006; Bhatnagar et al., 2011). Most of the developed adsorbents are tested only under laboratory conditions. Thus, there is an urgent need to develop a tailor-made low cost sustainable technology for fluoride removal. Water purification using biochar is relatively a new practice (Ahmad et al., 2014; Liu and Zhang, 2009; Mohan et al., 2007, 2011a, 2012, 2014a,b; Oh et al., 2012; Rajapaksha et al., 2014). Biochars have been made by biomass slow pyrolysis (Rajapaksha et al., 2014), fast pyrolysis (Brewer et al., 2009; Mohan et al., 2007, 2011a), and gasification (Brewer et al., 2009).

Fast pyrolysis biochars were successfully utilized for fluoride removal (Mohan et al., 2012). In the present investigation, corn stover slow pyrolysis biochar was used as a sustainable adsorbent for water defluoridation. The advantage of corn stover utilization is its wide abundance and low cost (Graham et al., 2007). Corn residues including cobs, leaves and stalks are abundantly available renewable materials. These have tremendous potential and can be used as an energy source in combustion, pyrolysis (slow and fast) and gasification processes (Mullen et al., 2010; Zhang et al., 2012). Lignocellulosic parts of corn plants can be utilized to produce slow pyrolysis biochar for fluoride removal from water. Furthermore,

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magnetic filtration is an emerging water treatment technology which can provide rapid, efficient contaminants removal from water. Inexpensive magnetic biochar adsorbents could be developed for fluoride removal and exhausted magnetic biochar can easily be separated from solution using a simple magnetic separator. Therefore, corn stover biochar (CSBC) and magnetic corn stover biochar (MCSBC) were produced, characterized and used for fluoride removal from water.

Batch fluoride removal studies at different temperatures and biochar doses were carried out to obtain the required kinetic and equilibrium data for the design of fixed-bed reactors. Kinetic data were fitted and compared using the Lagergren first-order (Lagergren, 1898) and pseudo-second order (Ho, 2006) rate equations. Fluoride sorption data were described by Freundlich (1906), Langmuir (1916), Redlich and Peterson (1959), Sips (1948), Radke and Prausnitz (1972), Toth (1971) and Koble and Corrigan (1952) mathematical models in order to perform the fixed-bed calculations.

The Freundlich or van Bemmelen equation (Freundlich, 1906; Weber, 1972) does not indicate an equilibrium uptake capacity of the adsorbent. Therefore, it can only reasonably be applied in the low to intermediate concentration range. The nonlinear Freundlich model is given by Eq. (1).

$$q_e = K_F C_e^{1/n} \tag{1}$$

where q_e is the amount of fluoride adsorbed per unit weight of biochar (mg/g), C_e is the fluoride equilibrium concentration in the bulk solution (mg/L), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ is the constant representing the adsorption intensity.

Langmuir equation (Langmuir, 1916; Weber, 1972) is applicable for single-layer adsorption. It also provides information on uptake capabilities and also reflects the usual equilibrium process behavior. The nonlinear Langmuir equation is given by Eq. (2).

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \tag{2}$$

where q_e is the amount of fluoride adsorbed per unit weight of biochar (mg/g), C_e is the equilibrium concentration of fluoride in the bulk solution (mg/L), Q^0 is the monolayer adsorption capacity (mg/g) and b is the constant which is related to the energy or net enthalpy, H, of adsorption, ($b \propto e^{-\Delta H/RT}$).

The Redlich–Peterson equation (Redlich and Peterson, 1959) incorporates three parameters where the exponent, β_{RP}, lies between 0 and 1.

$$q_e = \frac{K_{RP} C_e}{(1 + a_{RP} C_e \beta_{RP})} \tag{3}$$

where K_{RP}, a_{RP} and β_{RP} are Redlich–Peterson isotherm constants and the exponent, β_{RP}, lies between 0 and 1.

For $\beta = 1$, it reduces to Langmuir adsorption isotherm.

$$q_e = \frac{K_{RP} C_e}{(1 + a_{RP} C_e)} \tag{4}$$

When $\beta = 0$, it becomes Henry's equation.

$$q_e = \frac{K_{RP} C_e}{(1 + a_{RP})} \tag{5}$$

The Langmuir-Freundlich or Sips equation (Sips, 1948) (Eq. (6)) is a combined form of Langmuir and Freundlich models derived for predicting the heterogeneous adsorption systems (Foo and Hameed, 2010). At low concentrations, this equation effectively reduces to a Freundlich isotherm and thus, does not obey Henry's law. At high adsorbate concentrations, it predicts a monolayer sorption capacity characteristic of Langmuir isotherm.

$$q_e = \frac{K_{LF} C_e n_{LF}}{1 + (a_{LF} C_e) n_{LF}} \tag{6}$$

where K_{LF}, a_{LF} and n_{LF} are the Sips constants.

Radke and Prausnitz model (Radke and Prausnitz, 1972) (Eq. (7)) was developed using thermodynamic considerations. This model is applicable in the wide range of concentrations. The correlation of Radke–Prausnitz isotherm is usually characterized by the high RMSE and chi-square values (Foo and Hameed, 2010).

$$q_e = \frac{a\, b\, C_e^{\beta}}{a + b C_e^{\beta - 1}} \tag{7}$$

where a, b and β are the Radke and Prausnitz isotherm constants.

The Toth isotherm model (Eq. (8)) (Toth, 1971) is an improved Langmuir isotherm model useful in describing heterogeneous adsorption systems satisfying both low and high-end boundary of the concentration (Foo and Hameed, 2010)

$$q_e = \frac{K_T C_e}{(1 + B_T C_e \beta_T)^{1/\beta_T}} \tag{8}$$

where K_T, B_T and β_T are the Toth constants.

The Koble–Corrigan isotherm (Koble and Corrigan, 1952) is a three-parameter equation (Eq. (9)), which incorporated both Langmuir and Freundlich isotherm models for representing the equilibrium adsorption data.

$$q_e = \frac{A C_e n_{KC}}{1 + (b C_e) n_{KC}} \tag{9}$$

where A, b and n_{KC} are the Koble–Corrigan isotherm constants.

2. Methods

All chemicals were either AR or GR-grades. Ferric sulfate (>96%), ferrous sulfate (99.5%), and sodium hydroxide (98%) were purchased from Merck, India. A stock solution of fluoride (1000 mg/L) was made by dissolving sodium fluoride (NaF) in doubly-distilled water. The pH measurements were made using a pH meter (Model EUTECH, pH510). The pH of test solutions were adjusted using HNO_3 (0.1 N) and NaOH (0.1 N). Agitation of biochar and fluoride samples was carried out using two water bath incubator shakers (models RC51000 and MSW-275). A Mettler Toledo balance (model AB 265-S/FACT) was used for weighings.

2.1. Biochar feedstock preparation

The corn stover biomass was obtained from Chandni Chowk, New Delhi, India [28°39.44′(N) 77°13.19′(E)]. The moisture content was reduced to <10% by air drying for 1–2 days. The dried biomass was cut into small pieces (particle size: 10–15 mm) and used to prepare biochar in an indigenously designed pyrolysis reactor.

2.2. Reactor and production method

The corn stover was pyrolyzed at 500 °C in a stainless steel cylindrical vessel (180 mm long and 75 mm internal diameter) as shown in the schematic (Fig. 1) fitted inside the muffle furnace. The vessel was connected to a glass condenser for biooil collection (Fig. 1). The reactor vessel was tightly packed with corn stover (~100 g). Furthermore, corn stover was purged with an inert gas in the reaction vessel prior to heating in the muffle furnace. Biomass pyrolysis at 500 °C was carried out for a residence time of 30 min. After 30 min, the muffle furnace was turned off and cooled for 20 h. Char was collected in the sealed vessel. The collected char was sieved. The biochar fractions of 30–50, 50–100, 100–200 mesh sizes (595–297, 297–149, 149–74 micron dia.) were collected and

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